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Synthesis and properties of 3-arylcyclohepta[4,5]imidazo[1,2-*a*]-1,3,5-triazine-2,4(3*H*)-diones and related compounds: photo-induced autorecycling oxidation of some amines

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Abstract—Novel 3-phenyl- and 3-(4-nitrophenyl)cyclohepta[4,5]imidazo[1,2-*a*]-1,3,5-triazine-2,4(3*H*)-diones and the corresponding imino derivatives **5a**,**b** and **6a**,**b** were synthesized in modest to moderate yields by the abnormal and normal aza-Wittig reaction of 2-(1,3-diazaazulen-2-ylimino)triphenylphosphorane with aryl isocyanates and subsequent heterocyclization reaction with a second isocyanate. The related cationic compound, 1-methyl-3-phenylcyclohepta[4,5]imidazo[1,2-*a*]-1,3,5-triazine-2,4(3*H*)-dionylium tetrafluoroborate **7a**, was also prepared. The electrochemical reduction of these compounds exhibited more positive reduction potentials as compared with those of the related compounds of 3,10-disubstituted cyclohepta[4,5]pyrrolo[2,3-*d*]pyrimidine-2,4(1*H*,3*H*)-dione systems. In a search of the oxidizing ability, compounds **5a**, **6a**, and **7a** were demonstrated to oxidize some amines to give the corresponding imines in more than 100% yield under aerobic and photo-irradiation conditions, while even benzylamine was not oxidized under aerobic and thermal conditions at 100 °C. The oxidation reactions by cation **7a** are more efficient than that by **5a** and **6a**. Quenching of the fluorescence of **5a** was observed, and thus, the oxidation reaction by **5a** probably proceeds via electron-transfer from amine to the excited singlet state of **5a**. In the case of cation **7a**, the oxidation reaction is proposed to proceed via formation of an amine-adduct of **7a** and subsequent photo-induced radical cleavage reaction.

1. Introduction

The importance of fused pyrimidines, which are common sources for the development of new potential therapeutic agents,[1,2] is well known. Among these, flavins are known to play an important role as cofactors in a wide variety of biological redox reactions. Dehydrogenation reactions represent a major family of processes mediated by the subclass of flavoenzymes known as oxidase. Included in this group are the oxidative transformations of alcohols to carbonyl compounds, of amines to imines, and of fatty acid esters to their α,β-unsaturated analogs[3]. In this context, 5-deazaflavin (**1**) has been studied extensively in both enzymatic[4] and model systems[5,6] in the hope of gaining mechanistic insight into flavin-catalyzed reactions. On the basis of the above observations and our interest concerning the unique reactivity afforded by the vinyliminophosphoranes[7] and related compounds,[8] we have previously studied convenient preparations of 1,3-dialkylcyclohepta[4,5]pyrrolo[2,3-*d*]pyrimidine-2,4(1*H*,3*H*)-diones (**2**)[9] and 3.10-disubstituted cyclohepta[4,5]pyrrolo[2,3-*d*]pyrimidine-2,4(3*H*,10*H*)-diones (**3**) and derivatives,[10] which are the structural isomers of 5-deazaflavin (**1**) (Fig. 1). Cationic

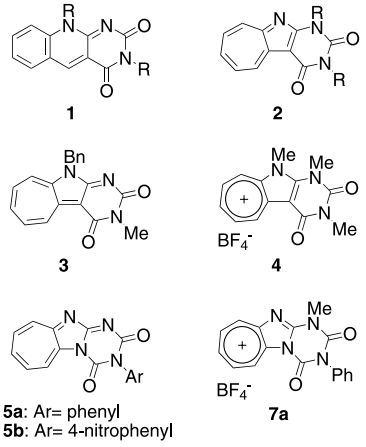

Figure 1.

Keywords: 3-Arylcyclohepta[4,5]imidazo[1,2-*a*]-1,3,5-triazine-2,4(3*H*)-diones; aza-Wittig reaction; X-ray analysis; Photo-induced autorecycling oxidation.
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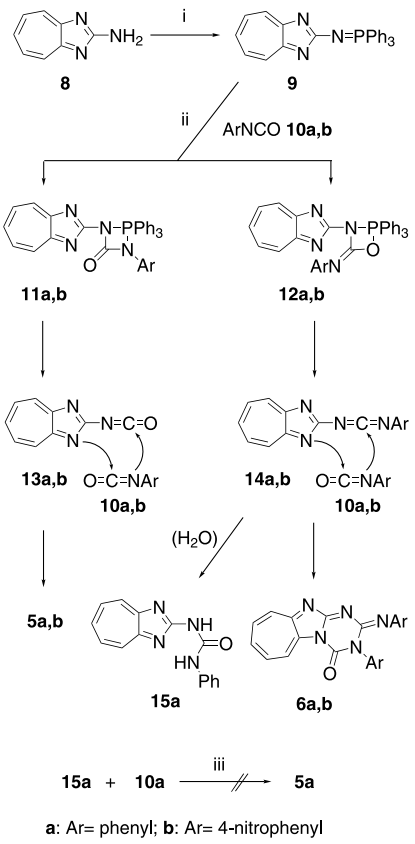


Scheme 1. Reagents and conditions: (i) PPh_3, DEAD, THF, rt, 4 h; (ii) benzene or toluene, reflux; (iii) $ZnCl_2$, dioxane, reflux, 50 h.

compounds **4** have also been prepared.[11] Compounds **3** and **4** have an appreciable oxidizing ability toward some alcohols and/or amines under photo-irradiation and aerobic conditions in an autorecycling process.[11,12] Thus, structural modifications of the uracil-annulated heteroazulenes such as **2**, **3**, and **4** are an interesting project in view of the exploration of novel functions. Much of the motivation for studying the properties of organic molecules stems from manipulation of the primary chemical structure. Although strategies for raising or lowering the HOMO and LUMO levels include conjugation length control, the introduction of an electron-withdrawing or donating group or element to the parent molecular skeleton is also an interesting project. Based on this concept, we studied here the synthesis, structural characteristics, and electrochemical properties of 3-arylcyclohepta[4,5]imidazo[1,2-*a*]-1,3,5-triazine-2,4(3*H*)-diones (**5a**,**b**) and related compounds **6a**,**b**, which involve the 1,3-diazaazulene and triazinedione skeletons instead of a 1-azaazulene and a pyrimidinedione ring system, along with cationic compound **7a** (Fig. 1). Photo-induced and thermal autorecycling oxidation of some amines to give the corresponding imines is studied as well. We describe here the results in detail.

2. Results and discussion

2.1. Synthesis

The aza-Wittig reaction of iminophosphoranes with isocyanate has proven to be one of the most useful methodologies for the synthesis of nitrogen-containing heterocycles.[7,8,13] We report herein an abnormal aza-Wittig reaction observed in the attempted program directed toward the synthesis of **5a**,**b** along with the corresponding imines **6a**,**b**. The abnormal aza-Wittig reaction involves the formation of an isocyanate instead of a carbodiimide intermediate, and reported studies on this reaction are very limited.[14] Starting from the 2-amino-1,3-diazaazulene (**8**),[15] the iminophosphorane (**9**) was prepared under Mitsunobu conditions using DEAD and triphenylphosphine (Scheme 1).[16] Treatment of the iminophosphorane (**9**) with phenyl and 4-nitrophenyl isocyanates (**10a**,**b**) afforded **5a**,**b** and **6a**,**b**, along with the known compound *N*-(1,3-diazaazulen-2-yl)-*N*′-phenylurea (**15a**).[17] Reaction conditions and the yields of the products are summarized in Table 1. The structures of new compounds **5a**,**b** and **6a**,**b** are confirmed on the basis of the ^{1}H (Table 2) and ^{13}C NMR spectra, IR, UV–vis, and mass spectral data, as well as elemental analyses. In addition, while single crystals of **5a**,**b** were not obtained, the structural characteristics of **6a**,**b** are revealed by the X-ray crystal analysis (vide infra). The proposed mechanistic pathways for the formation of **5a**,**b** and **6a**,**b** are outlined in Scheme 1. Both intermediates **11a**,**b** and **12a**,**b** can be formed upon treatment of **9** with **10a**,**b**. Breakdown of **11a**,**b** involving loss of triphenylphosphinimide results in the isocyanate intermediates **13a**,**b** as the abnormal aza-Wittig product. The isocyanates **13a**,**b** can undergo an intermolecular heterocyclization reaction with a second aryl isocyanates **10a**,**b** providing compounds **5a**,**b**. In contrast, intermediates **12a**,**b** can lead to the carbodiimides **14a**,**b** as the normal aza-Wittig product involving the loss of triphenylphosphine oxide. Subsequent heterocyclization of **14a**,**b** with a second aryl isocyanate **10a**,**b** results in the formation of compounds **6a**,**b**. The isocyanate **14a** reacts also with stray water to give the urea **15a**. The controlling factor for the abnormal and normal aza-Wittig reactions is still unclear. 2-Amino-1-azaazulene is known to react with **10a** to give *N*-(1-azaazulen-2-yl)-*N*′-phenylurea, which undergoes heterocyclization with a second **10a** to give 3-phenylcyclohepta[4,5]pyrrolo[1,2-*a*]-1,3,5-triazine-2,4-(3*H*)-dione.[18] In contrast, the urea **15a**, which was obtained upon treatment of **8** with **10a**, does not react with a second isocyanate **10a**, and the expected **5a** was not obtained even in the presence of $ZnCl_2$. Thus, the iminophosphorane (**9**) is a key synthon for the formation of the desired ring system of **5a**,**b**. In relation to the studies of the oxidizing ability of neutral and cationic compounds such as **3** and **4**, compound **5a** was converted to **7a** upon treatment of **5a** with MeI and followed by counter ion exchange reaction by using 42%

Table 1. Results for the reaction of **9** with aryl isocyanates **10a**,**b**

Isocyanate	Solvent[a]	Time/h	Product (yield/%)		
10a	Benzene	58	**5a** (9)	**6a** (55)	**15a** (11)
10a	Toluene	20	**5a** (28)	**6a** (52)	**15a** (14)
10b	Toluene	24	**5b** (13)	**6b** (57)	

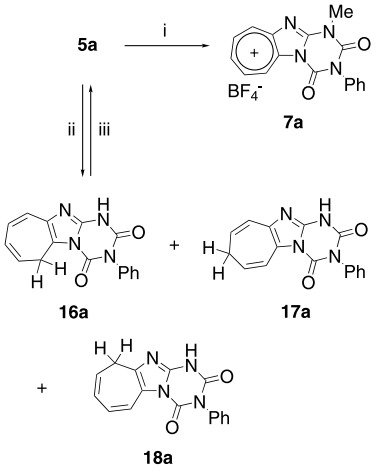
[a] Reaction was carried out under reflux.

Table 2. ^{1}H NMR spectral data (600 MHz) of **5a**,**b**, **6a**,**b**, and **7a** and reference compounds **3** and **4**

Compd		H5	H6	H7	H8	H9	Remaining signals
5a[a]	δ_H	9.17	8.19	8.06	8.32	8.45	7.36 (2H, d, J=8.2 Hz), 7.45 (1H, t, J=7.4 Hz), 7.52 (2H, d, J=8.2, 7.4 Hz)
	J	9.8	10.5	9.6	10.5		
5b[a]	δ_H	9.19	8.23	8.10	8.35	8.49	7.70 (2H, d, J=9.0 Hz), 8.39 (2H, d, J=9.0 Hz)
	J	9.8	9.8	9.2	10.5		
6a	δ_H	8.85	7.88	7.46	7.61	7.99	6.96 (1H, t, J=7.5 Hz), 7.04 (2H, d, J=8.3 Hz), 7.21 (2H, dd, J=8.3 Hz, 7.5), 7.41 (2H, d, J=8.1 Hz), 7.44 (1H, t, J=7.6 Hz), 7.54 (2H,dd, J=8.2, 7.6 Hz)
	J	11.2	10.8	10.1	9.8		
6b[a]	δ_H	9.00	7.84	7.92	7.99	8.19	7.13 (2H, d, J=8.9 Hz), 7.62 (2H, d, J=8.9 Hz), 8.12 (2H, d, J=8.9 Hz), 8.43 (2H, d, J=8.9 Hz)
	J	9.8	10.5	9.5	10.6		
7a[b]	δ_H	9.98–10.0	8.80–8.95			9.16	3.83 (3H, s), 7.44–7.48 (2H, m), 7.61–7.67 (2H, m)
	J	m	m		10.3		
3[c]	δ_H	9.29	7.66–7.90				5.69 (3H, s), 5.69 (2H, s), 7.26–7.3 (5H, m, Ph)
	J	10.6		m			
4[d]	δ_H	9.84–9.89	8.46–8.58			8.90–8.94	3.41 (3H, s), 3.94 (3H, s)
	J	m	m			m	

[a] Recorded in DMSO-d_6.
[b] Recorded in CD_3CN.
[c] Ref. 12.
[d] Ref. 11.

HBF_4 in Ac_2O in good yield. The spectroscopic data involving mass spectral data as well as the elemental analysis are in good accordance with the proposed structure. The redox ability of **5a** was also investigated. The reduction of **5a** with $NaBH_4$ was carried out to give a mixture of three regio-isomers **16a**, **17a**, and **18a**. The mixture of the regio-isomers was not separated, and thus, the structural assignment was based on the high resolution MS spectrum of the mixture and the ^{1}H NMR spectrum of each compounds, which was assigned independently by using the H–H Cosy spectrum. The mixture was oxidized by DDQ or under aerobic conditions to regenerate **5a**, and thus, the correlation of the compounds between **5a** and **16a**, **17a**, and **18a** was assessed (Scheme 2).



Scheme 2. Reagents and conditions: (i) (a) MeI, $(CH_2Cl)_2$, 100 °C, 3 h; (b) 42% aq. HBF_4, Ac_2O, 0 °C, 1 h; (ii) $NaBH_4$, MeOH, rt, 0.5 h; (iii) air, CH_2Cl_2, 7 days or DDQ, CH_2Cl_2, rt, 1 h.

2.2. Properties

The ^{1}H NMR spectra of two series of **5a**,**b** and **6a**,**b** resemble each other, respectively. Unambiguous proton assignment was successfully made, and the chemical shifts of the protons of the seven-membered ring and the aryl group and selected coupling constants are listed in Table 2, together with those of the reference compounds **3**[10] and cation **4**.[11] The chemical shifts of the seven-membered ring protons (H6–H9) of **5a** and **5b** are found in the appreciably lower field (δ 8.06–8.46 and δ 8.11–8.49) as compared with those (δ 7.66–7.90) of **3**. This feature is similarly observed in the chemical shifts of compounds **6a** (δ 7.46–7.99) and **6b** (δ 7.84–8.19). The chemical shifts of the seven-membered ring protons of cation **7a** are also listed and they are similar to those of cation **4**. In particular, the characteristic H5 signals appearing at around δ 9.0–9.9 in the ^{1}H NMR spectra of the compounds listed in Table 2 are due to the anisotropy effect of the oxygen atom of the triazinedione and pyrimidinedione moieties. The vicinal coupling constants of protons of the seven-membered ring of neutral compounds **5a**,**b** and **6a**,**b** suggest bond alternation in the cycloheptatriene moiety, while no significant bond alternation is observed in cation **7a** as well as **4**. The π-electron delocalization of cation **7a** is much enhanced as compared

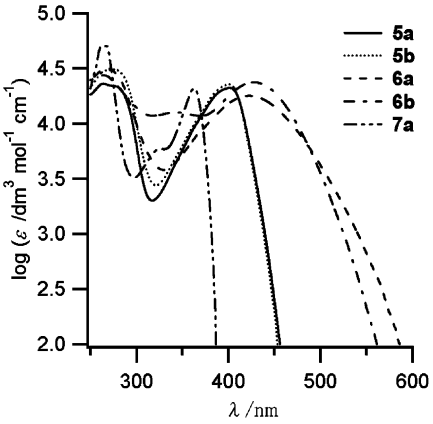


Figure 2. UV–vis spectra of **5a**,**b**, **6a**,**b** and **7a**.

with that of **5a**,**b** and **6a**,**b**. The UV–vis spectra of compounds **5a**,**b**, **6a**,**b** and cation **7a** in CH_3CN are shown in Figure 2. The two series of **5a**,**b** and **6a**,**b** are very similar to each other, respectively. On the other hand, the spectrum of cation **7a** exhibits a greater extent of blue-shift as compared with compound **5a**, suggesting the much lowering of the HOMO as compared with the LUMO by methylation.

Table 3. pK_{R+} values and reduction potentials[a] of **5a**,**b**, **6a**,**b**, **7a**[b] and reference compounds **3** and **4**

Compd	pK_{R+}	Reduction potential (V)[a] $E1_{red}$
5a	—	−1.15
5b	—	−1.12
6a	—	−1.24
6b	—	−1.14
7a	6.8	−0.66
3[b]	—	−1.37
4[c]	11.2	−0.87

[a] Peak potential in V versus $Ag/AgNO_3$.
[b] Ref. 10.
[c] Ref. 11.

The affinity of carbocation toward the hydroxide ion, expressed by the pK_{R+} value, is the common criterion of carbocation stability.[19] The value of cation **7a** was determined spectrophotometrically as 6.8 in buffer solutions prepared in 50% CH_3CN and indicated in Table 3, along with that of reference cation **4**. The value indicates that cation **7a** is much more unstable than reference compound **4**. The reduction potentials of **5a**,**b**, **6a**,**b**, and **7a** are determined by cyclic voltammetry (CV) in CH_3CN. The reduction waves of **5a**,**b**, **6a**,**b** and **7a** are irreversible under conditions of the CV measurements, and thus, their peak potentials are summarized in Table 3, together with those of the reference compounds **3**[10] and **4**.[11] As expected, the $E1_{red}$ of phenyl-substituted compounds **5a** and **6a** is more negative than that of 4-nitophenyl substituted derivatives **5b** and **6b**, respectively, due to the electron-withdrawing property of the 4-nitrophenyl group. The $E1_{red}$ of dicarbonyl compounds **5a**,**b** is more positive than that of the imino derivatives **6a**,**b**, respectively, due to the electron-withdrawing dicarbonyl function. The $E1_{red}$ of these compounds is less negative than that of the reference compound **3**. In contrast, the $E1_{red}$ of cation **7a** is much more positive than that of **5a**,**b** and **6a**,**b**, and the value is more positive than that of the reference compound **4**, suggesting an appreciable oxidizing property.

The X-ray structure analyses were carried out and the ORTEP drawings of **6a**,**b** are shown in Figure 3. The selected bond lengths and bent angles of the two aryl groups

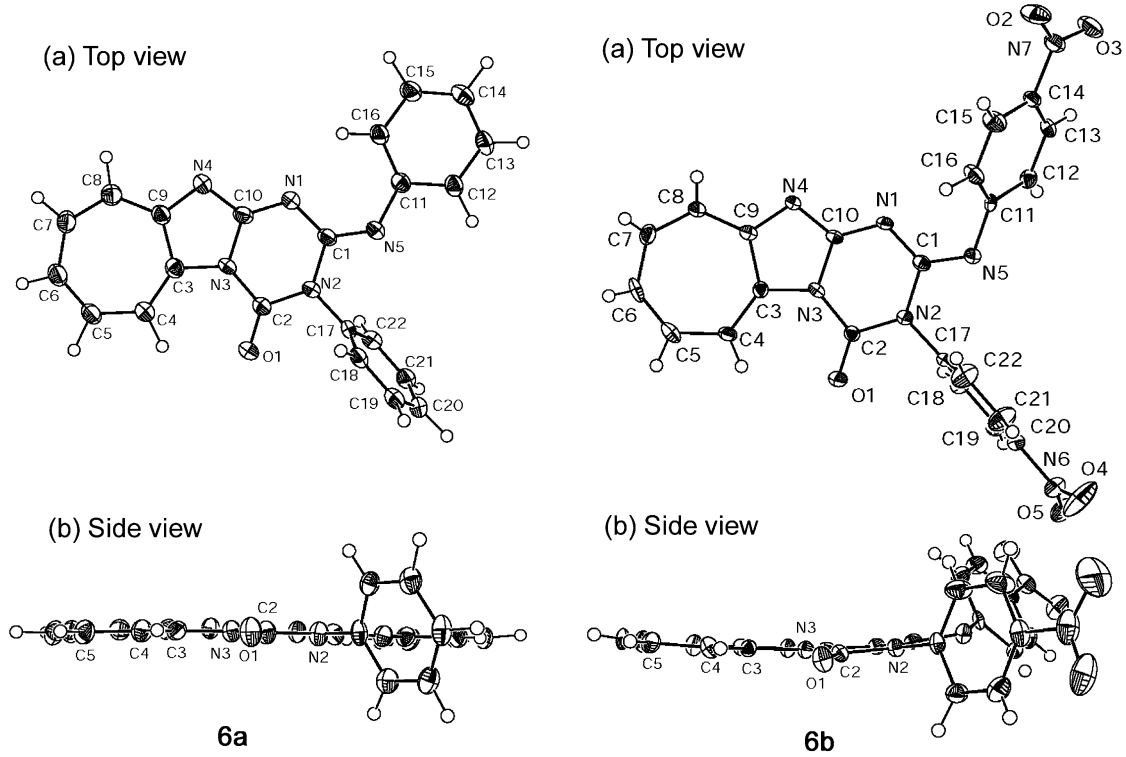


Figure 3. ORTEP drawings of **6a**,**b** with thermal ellipsoid plot (50% probability).

Table 4. Bond lengths of **6a**,**b** obtained by X-ray structure analysis

Compd.	Bond length[a]/Å												
	C3–C4	C4–C5	C5–C6	C6–C7	C7–C8	C8–C9	N4–C9	N4–C10	C3–N3	C10–N3	N1–C10	N1–C1	C1–N2
6a	1.38	1.40	1.35	1.41	1.37	1.40	1.34	1.34	1.38	1.39	1.30	1.35	1.43
6b	1.37	1.41	1.36	1.41	1.37	1.41	1.34	1.34	1.40	1.40	1.30	1.36	1.43

[a] Numbering is based on the ORTEP drawings in Figure 3.

from the plane of the 7–5–6 π-systems are summarized in Tables 4 and 5. The bond lengths of C3–C4, C5–C6, and C7–C8 are shorter than those of C4–C5 and C6–C7, suggesting bond-length alternation in the seven-membered ring as demonstrated by vicinal coupling constants of the ^{1}H NMR spectrum (Table 2). Electron delocalization in the triazine ring is not observed. Both 7–5–6 π-systems of **6a**,**b** are a nearly planar structure. The twisted angles of the aryl group against the plane of the 7–5–6 ring system are summarized in Table 5. The planes of the aryl group on the amide nitrogens of **6a**,**b** (N2Ar) are twisted 75.7 and 77.9°, respectively, against the plane of the 7–5–6 π-system. This is probably due to steric hindrance between the aryl group and the carbonyl-oxygen and imino-nitrogen. Remarkably, the twisted angle of N5Ar of **6a**,**b** is 2.5 and 58.7°, respectively (Table 1).

Table 5. Torsion angles of **6a**,**b** twisted angle/degree

Compd	N2Ar[a]	N5Ar[a]
6a	75.7	2.5
6b	77.9	58.7

[a] Numbering is based on the ORTEP drawings in Figure 3.

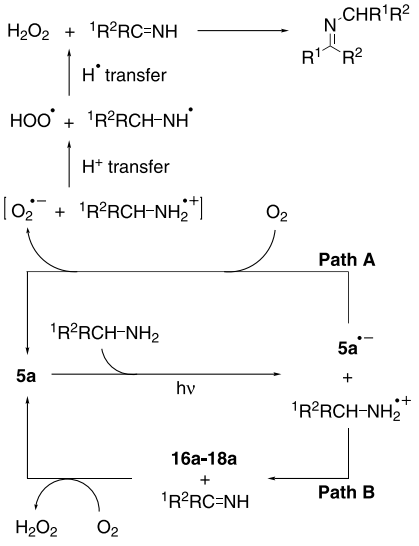
2.3. Photo-induced autorecycling oxidation

Compounds **3**,[12] **4**,[11] and related compounds[20] undergo photo-induced autorecycling oxidation toward some alcohols and some amines under aerobic conditions. In this context, we examined the oxidation of some amines by using **5a**, **6a**, and **7a** under aerobic and photo-irradiation (RPR100, 350 nm lamps) conditions. Although benzyl alcohol was not oxidized effectively by either **5a** or **7a**, we found that both compounds have oxidizing ability toward benzylamine, 1-phenylethylamine, hexylamine, and cyclohexylamine. In the amine oxidation, imine is produced at first; however, it reacts with another amine to result in the formation of another imine $R^1R^2C{=}N{-}CHR^1R^2$ and NH_3 (Scheme 3). Then the reaction mixture was diluted with ether and filtered and the filtrate was treated with 2,4-dinitrophenylhydrazine in 6% HCl to give 2,4-dinitrophenylhydrazone of the corresponding carbonyl compound. Direct irradiation of amines in the absence of **5a**, **6a**, and **7a** (named 'blank') gives the corresponding carbonyl compounds in low to modest yields under similar conditions. Thus, the yields are calculated by subtraction of the 'blank' yield from the total yield of the carbonyl compound in the presence of **5a** and **7a**, and the results are summarized in Table 6 (Entries 1–8). More than 100% yields are obtained based on **5a** and **7a**, and thus, autorecycling oxidation clearly proceeds. In contrast, oxidation reaction by using **6a** does not proceed effectively, and even benzylamine and 1-phenethylamine are oxidized in low yield as compared

Table 6. Photo-induced autorecycling oxidation of some amines by **5a**, **6a**, and **7a**[a]

Entry	Compd	Amines	Yield (%)[b,c]	Recycling no.
1	**5a**	$PhCH_2NH_2$	8322	83.2
2	**5a**	$PhCH(Me)NH_2$	6733	67.3
3	**5a**	Hexylamine	2000	20.0
4	**5a**	Cyclohexylamine	862	8.6
5	**7a**	$PhCH_2NH_2$	11 818	118.2
6	**7a**	$PhCH(Me)NH_2$	8457	84.6
7	**7a**	Hexylamine	3143	31.4
8	**7a**	Cyclohexylamine	909	9.1
9	**6a**	$PhCH_2NH_2$	909	9.1
10	**6a**	$PhCHMeNH_2$	400	4.0

[a] CH_3CN solution was irradiated by RPR100, 350 nm lamps.
[b] Isolated by converting to the corrresponding 2,4-dinitrophenylhydrazone.
[c] Based on the compound used; the yield is calculated by subtraction of the 'blank' yield from the total yield.



Scheme 3.

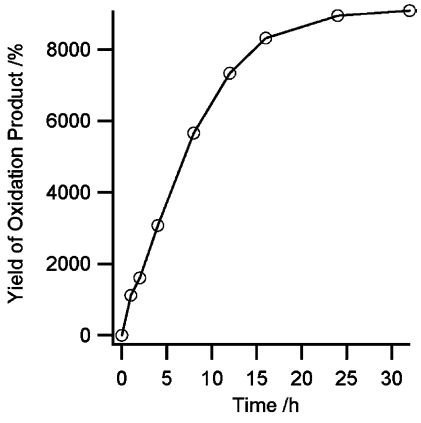


Figure 4. Time dependence of benzylamine oxidation by **5a**.

with that of **5a** and **7a** (Table 6, Entries 9 and 10). As the time of photo-irradiation is prolonged, the yield of oxidation product by **5a** is increased gradually. After 16 h irradiation, the yield is not increased appreciably (Fig. 4), suggesting plausible decomposition of **5a**. The attempted oxidation reaction of benzylamine by **5a** was not observed under thermal and aerobic conditions. In a previous study, the fluorescence spectrum of 1,3-dimethylcyclohepta[*b*]furo-[2,3-*d*]pyrimidine-2,4(1*H*,3*H*)-dionylium tetrafluoroborate, which has oxidizing ability toward some alcohols, is quenched by addition of 1-phenylethanol, suggesting an interaction of the singlet excited state of the compound with the alcohol.[21] Thus, in a search of the mechanistic aspect of the photo-induced oxidation reaction, the fluorescence spectra of **5a** and **7a** were studied; the quantum yield (Φ) of that for **5a** was determined to be 0.075; however, no fluorescence spectra of **7a** was observed. The fluorescence spectrum of **5a** (Fig. 5) was quenched by adding benzylamine, while quenching of the fluorescence was not observed by addition of benzyl alcohol, suggesting interaction of the singlet excited state of **5a** with the amine.

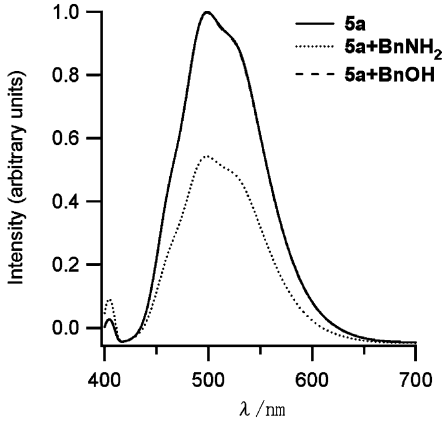


Figure 5. Fluorescence spectra of **5a**.

The postulated mechanistic pathways for the oxidation of amines ($R^1R^2CHNH_2$) are depicted in Scheme 3. The electron transfer from amines to the excited singlet state of **5a** would occur to produce a radical anion $\mathbf{5a}^{\cdot -}$ and $R^1R^2CHNH_2^{\cdot +}$. In the presence of oxygen, an electron transfer from $\mathbf{5a}^{\cdot -}$ to O_2 may give the radical ion pair [$R^1R^2CHNH_2^{\cdot +}$ $O_2^{\cdot -}$] and **5a**. Then a proton transfer from $R^1R^2CHNH_2^{\cdot +}$ to $O_2^{\cdot -}$ may occur, followed by formation of product $R^1R^2CH{=}NH$ and H_2O_2 (Path A).[22] On the other hand, there is an alternative pathway (Path B), in which a mixture of hydrogenated compounds **16a**, **17a**, and **18a** (Scheme 3) in addition to the imine are generated from $\mathbf{5a}^{\cdot -}$ and $R^1R^2CH{-}NH_2^{\cdot +}$ directly; the former compound is oxidized under aerobic conditions to regenerate **5a**. It is shown that the regeneration of **5a** by air oxidation of **16a**, **17a**, and **18a** is slow and seems to be ineffective to achieve an efficient autorecycling oxidation (Scheme 2, vide supra). Thus, Path A seems to be favorable. In the case of oxidation by **7a**, photo-induced homolytic cleavage of the initially formed amine-adduct of **7a**, which is detected by UV–vis spectra as shown in Figure 6, probably occurs to generate $\mathbf{7a}^{\cdot}$ and $R^1R^2CHNH_2^{\cdot +}$. An electron transfer from $\mathbf{7a}^{\cdot}$ to O_2 gives the radical ion pair [$R^1R^2CHNH_2^{\cdot +}$ $O_2^{\cdot -}$] and **7a**; the former ion pair would follow Path A.

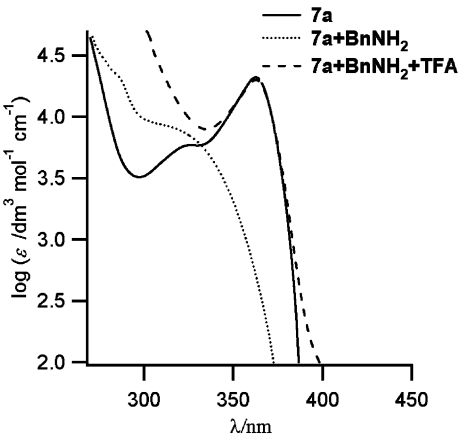


Figure 6. UV–vis spectra of **7a**.

3. Conclusion

Novel 3-phenyl- and 3-(4-nitropenyl)cyclohepta[4,5]-imidazo[1,2-*a*]-1,3,5-triazine-2,4(3*H*)-diones and the corresponding imino derivatives **5a**,**b**, **6a**,**b**, and 1-methyl-3-phenylcyclohepta[4,5]imidazo[1,2-*a*]-1,3,5-triazine-2,4-(1*H*,3*H*)-dionylium tetrafluoroborate **7a** were synthesized in modest to moderate yields. Compounds **5a**, **6a**, and **7a** were demonstrated to oxidize some amines to give the corresponding imines in more than 100% yield under aerobic and photo-irradiation conditions. Thus, oxidation reaction proceeds in a photo-induced autorecycling process.

4. Experimental

4.1. General

IR spectra were recorded on a HORIBA FT-710 spectrometer. UV–vis spectra were recorded on a Shimadzu UV-3101PC spectrometer. Mass spectra and high-resolution mass spectra were run on JMS-AUTOMASS 150 and JMS-SX102A spectrometers. Unless otherwise specified, ^1H NMR and ^{13}C NMR spectra were recorded on an AVANCE 600 spectrometer using $CDCl_3$ as the solvent, and the chemical shifts are given relative to internal $SiMe_4$ standard: *J*-values are given in Hz. Mps were recorded on a Yamato MP-21 apparatus and are uncorrected. Photo-irradiation was carried out by using RPR-100 fitted with 350 nm lamps though a Pyrex filter.

4.2. Preparation of 9

To a solution of **8** (435 mg, 3 mmol) and PPh_3 (786 mg, 3 mmol) in THF (30 mL) was added DEAD (1.5 mL, 3.3 mmol) at 0 °C, and the mixture was stirred at rt for 4 h. The reaction mixture was filtered, and the filtrate was concentrated. The resulting residue was crystallized from Et_2O to give **9** (1.17 g, 86%).

4.2.1. 2-(1,3-Diazaazulen-2-yl)iminotriphenylphosphorane (9). Pale yellow prisms; mp 212–213 °C (decomp.) (from AcOEt); ^{1}H NMR (600 MHz) δ 7.31 (1H, t, J=9.9 Hz, H-6), 7.44 (6H, ddd, J=7.8, 7.5, 2.9 Hz, *m*-Ph), 7.53 (3H, td, J=7.5, 1.7 Hz, *p*-Ph), 7.58 (2H, dd, J=10.7, 9.9 Hz, H-5 and H-7), 7.93 (6H, dd, J=7.8, 1.7 Hz, *o*-Ph), 7.94 (2H, d, J=10.7 Hz, H-4 and H-8); ^{13}C NMR (150.9 MHz) δ 124.6 (C-4 and C-8), 128.5 (J_{PC}=12.2 Hz, *m*-Ph), 128.8 (J_{PC}=100.1 Hz, *i*-Ph), 129.4 (C-6), 132.1 (J_{PC}=2.6 Hz, *p*-Ph), 133.4 (J_{PC}=10.1 Hz, *o*-Ph), 133.6 (C-5 and C-7), 165.1 (C-2); ^{31}P NMR (109.3 MHz) δ 16.97; IR ($CHCl_3$, cm^{-1}) 1549, 1470, 1438, 1364, 1114, 957, 926, 882; MS *m*/*z* 406 (M^++H); Anal. calcd for $C_{26}H_{21}N_3P$: C, 77.02; H, 4.97; N, 10.36. Found: C, 76.87; H, 4.95; N, 10.46.

4.3. Preparation of 5a and 6a

A solution of **9** (810 mg, 2.0 mmol) and **10a** (714 mg, 6.0 mmol) in a solvent (100 mL) indicated in Table 1 was refluxed for an adequate time. After evaporation of the solvent, the residue was dissolved in CH_2Cl_2, the insoluble material was collected by filtration to give *N*-(1,3-diazaazuln-2-yl)-*N*′-phenylurea **15a**, and the filtrate was separated by column chromatography on SiO_2. The fractions eluted with AcOEt gave **6a**, and the fractions eluted with acetone gave **5a**. The results are summarized in Table 1.

4.3.1. 3-Phenylcyclohepta[4,5]imidazo[1,2-*a*]-1,3,5-triazine-2,4(3*H*)-dione (5a). Yellow needles; mp 228–230 °C (decomp.) (from CH_2CL_2/Et_2O); ^{13}C NMR (150.9 MHz, DMSO-d_6) δ 124.6, 128.2, 128.6, 128.9, 134.5, 135.6, 138.7, 139.0, 142.7, 145.1, 147.9, 155.0, 162.7, 166.3; IR (KBr, cm^{-1}) 1739, 1707; MS *m*/*z* 290 (M^+); Anal. calcd for $C_{16}H_{10}N_4O_2$–1/4H_2O: C, 65.19; H, 3.59; N, 19.01. Found: C, 65.20; H, 3.23; N, 19.14.

4.3.2. 3-Phenyl-2-phenyliminocyclohepta[4,5]imidazo[1,2-*a*]-1,3,5-triazine-4-one (6a). Dark red prisms; mp 222–223 °C (decomp) (from AcOEt); ^{13}C NMR (150.9 MHz) ^{13}C NMR (150.9 MHz) δ 122.2, 123.0, 123.1, 128.3, 128.5, 128.7, 129.5, 133.5, 135.7, 136.2, 137.9, 141.3, 146.1, 147.7, 148.0, 148.4, 159.7, 168.2; IR ($CHCl_3$, cm^{-1}) 1728; MS *m*/*z* 366 (M^++H); Anal. calcd for $C_{22}H_{15}N_5O$: C, 72.32; H, 4.14; N, 19.17. Found: C, 72.02; H, 4.12; N, 19.05.

4.4. Preparation of 5b and 6b

A solution of **9** (810 mg, 2.0 mmol) and **10b** (984 mg, 6.0 mmol) in toluene–dioxane (1/1; 100 mL) was refluxed for 24 h. After evaporation of the toluene, the residue was dissolved in CH_2Cl_2, the insoluble material was filtered and the filtrate was concentrated and separated by column chromatography on SiO_2. The fractions eluted with AcOEt afforded **6b**, and the fractions eluted with acetone gave **5b**. The results are summarized in Table 1.

4.4.1. 3-(4-Nitrophenyl)cyclohepta[4,5]imidazo[1,2-*a*]-1,3,5-triazine-2,4(3*H*)-dione (5b). Yellow powder; mp 249–252 °C (decomp.) (from AcOEt); ^{13}C NMR (150.9 MHz, DMSO-d_6) δ 124.5, 125.3, 130.7, 135.0, 139.4, 139.5, 141.8, 143.2, 145.2, 147.4, 147.9, 154.7, 163.0, 166.5; IR (KBr, cm^{-1}) 1746, 1683; MS *m*/*z* 336 (M^++H); Anal. calcd for $C_{16}H_9N_5O_4$–1/4CH_2Cl_2: C, 54.75; H, 2.69; N, 19.64. Found: C, 54.75; H, 2.80; N, 19.39.

4.4.2. 3-(4-Nitrophenyl)-2-(4-nitorophenyl)iminocyclohepta[4,5]imidazo[1,2-*a*]-1,3,5-triazine-4-one (6b). Red prisms; mp 258–260 °C (decomp.) (from $CHCl_3$); ^{13}C NMR (150.9 MHz, DMSO-d_6) δ 123.6, 123.8, 124.5, 124.9, 130.1, 134.6, 137.3, 138.4, 141.5, 142.1, 145.8, 147.2, 147.8, 149.3, 154.0, 160.1, 168.2, 175.2; IR ($CHCl_3$, cm^{-1}) 1734; MS *m*/*z* 456 (M^++H); Anal. calcd for $C_{22}H_{13}N_7O_5$–$CHCl_3$: C, 48.06; H, 2.46; N, 17.06. Found: C, 48.32; H, 2.58; N, 17.30.

4.5. Preparation of urea 15a

A solution of **8** (73 mg, 0.5 mmol) and **10a** (179 mg, 1.5 mmol), and $ZnCl_2$ (68 mg, 0.5 mmol) in dioxane (40 mL) was heated under reflux for 50 h. After evaporation of the solvent, the reaction mixture was washed with EtOH, the EtOH layer was concentrated to give **15a** (106 mg, 80%). A similar reaction in the absence of $ZnCl_2$ afforded **15a** (45 mg, 34%), which is identified on the basis of comparison of the physical data reported previously.[17]

4.6. Reaction of 15a with 10a

A mixture of **15a** (26 mg, 0.1 mmol) and **10a** (24 mg, 0.2 mmol) in the presence or absence of $ZnCl_2$ (14 mg, 0.1 mmol) in dioxane (40 mL) was heated under reflux for 50 h. The reaction mixture was concentrated and the residue was washed with EtOH. The collected EtOH solution was concentrated and **15a** was isolated in 83% (in the presence of $ZnCl_2$) and 76% (in the absence of $ZnCl_2$).

4.7. Preparation of 7a

A solution of **5a** (2.9 mg, 0.1 mL) and MeI (2 mL) in $(CH_2Cl)_2$ (4 mL) in a sealed tube was heated at 100 °C for 3 h. The solvent was evaporated and the residue was dissolved in Ac_2O (3 mL) and treated with 42% aq. HBF_4 (0.6 mL). To the solution was added ether (5 mL) and precipitates were collected by filtration to give **7a** (36 mg, 92%).

4.7.1. 1-Methyl-3-phenylcyclohepta[4,5]imidazo[1,2-*a*]-1,3,5-triazine-2,4(3*H*)-dionylium tetrafluoroborate (7a). Colorless needles; mp 289–291 °C (decomp.) (from CH_3CN/Et_2O.); ^{13}C NMR (150.9 MHz, CD_3CN) δ 32.1, 96.1, 128.7, 130.4, 130.7, 133.7, 134.8, 142.0, 145.0, 147.0, 147.2, 147.7, 148.2, 155.3, 162.8; IR ($CHCl_3$, cm^{-1}) 1726, 1084; MS *m*/*z* 305 (M^+−BF_4). HRMS calcd for $C_{17}H_{13}N_4O_2BF_4$: 305.1060 (M−BF_4). Found: 305.1021 (M^+−BF_4). Anal calcd for $C_{17}H_{13}N_4O_2BF_4$: C, 52.07; H, 3.34; N, 14.29. Found: C, 52.04, H, 3.53; N, 13.95.

4.8. Reduction of 5a

A solution of **5a** (29 mg, 0.1 mmol) and $NaBH_4$ (23 mg, 0.6 mmol) in MeOH (10 mL) was stirred at rt for 30 min. The reaction mixture was extracted with CH_2Cl_2 and the extract was dried over Na_2SO_4, and concentrated in vacuo.

The resulting residue afforded a mixture of **16a**, **17a**, and **18a** (100%) in a ratio of 6:3:1.

4.8.1. A mixture of 16a, 17a, and 18a. IR ($CHCl_3$, cm^{-1}) 1726, 1637, 1084; MS (FAB) m/z 293 ($M^+ + H$). HRMS calcd for $C_{16}H_{13}N_4O_2$: 293.1040 (M+H). Found: 293.1044 ($M^+ + H$).

4.8.2. Compound 16a. ^{1}H NMR (600 MHz) δ 3.73 (2H, d, J=6.4 Hz, H-6), 5.54 (1H, dt, J=10.4, 6.4 Hz, H-7), 6.11 (1H, dd, J=10.4, 6.1 Hz, H-8), 6.45 (1H, dd, J=11.5, 6.1 Hz, H-9), 6.90 (1H, d, J=1.5 Hz, H-10), 7.30–7.56 (5H, m, *o*-Ph, *m*-Ph and *p*-Ph); MS *m*/*z* 293 (M^+).

4.8.3. Compound 17a. ^{1}H NMR (600 MHz) δ 3.36 (2H, d, J=6.3 Hz, H-10), 5.48 (1H, dt, J=10.2, 6.3 Hz, H-10), 6.08–6.13 (1H, m, H-8), 6.40 (1H, dd, J=11.5, 6.1 Hz, H-7), 7.30–7.39 (1H, m, H-6), MS *m*/*z* 293 (M^+).

4.8.4. Compound 18a. ^{1}H NMR (600 MHz) δ 2.50 (2H, t, J=7.0 Hz, H-8), 5.36 (1H, dt, J=10.0, 7.0 Hz, H-7), 5.52–5.56 (1H, m, H-9), 6.87 (1H, d, J=10.0 Hz, H-10), 7.20 (1H, d, J=10.0 Hz, H-6), 7.30–7.56 (5H, m, *o*-Ph, *m*-Ph and *p*-Ph); MS *m*/*z* 293 (M^+).

4.9. Oxidation of a mixture of 16a, 17a, and 18a

A mixture of **16a**, **17a**, and **18a** (29 mg, 0.1 mmol) in CH_2Cl_2 (15 mL) was stirred under aerobic conditions for 7 day. The solution was dried over Na_2SO_4 and concentrated. The resulting residue was purified by TLC on SiO_2 (acetone) to give **5a** (17 mg, 59%).

A solution of **16a**, **17a**, and **18a** (29 mg, 0.1 mmol) and DDQ (27 mg, 0.12 mmol) in CH_2Cl_2 (15 mL) was stirred at rt for 1 h. The reaction mixture was extracted with CH_2Cl_2, and the extract was washed with aq. Na_2CO_3 and dried over Na_2SO_4. The CH_2Cl_2 was evaporated and the residue was purified by TLC on SiO_2 (acetone) to give **5a** (25 mg, 86%).

4.10. General procedure for the photo-induced auto-recycling oxidation of amines

To a solution of **5a** (0.005 mmol) and **7a** (0.005 mmol) in CH_3CN (16 mL) was added an amine (2.5 mmol) in a pyrex tube, and the mixture was irradiated by RPR-100, 350 nm lamps under aerobic conditions for 16 h. The reaction mixture was concentrated in vacuo and diluted with ether and filtered. The filtrate was treated with 2,4-dinitrophenylhydrazine in 6% HCl to give the 2,4-dinitrophenylhydrazone of the corresponding carbonyl compound. The results are summarized in Table 6. In the case of the benzylamine oxidation, nine samples are irradiated and time dependency of the yields of 2,4-dinitrophenylhydrazone was investigated as summarized in Figure 4.

4.11. Determination of pK_{R+} value of cation 7a

Buffer solutions of slightly different acidities were prepared by mixing aqueous solutions of potassium hydrogen phthalate (0.1 M) and HCl (0.1 M) (for pH 2.2–4.0), potassium hydrogen phthalate (0.1 M) and NaOH (0.1 M) (for pH 4.1–5.9), and KH_2PO_4 (0.1 M) and NaOH (0.1 M) (for pH 6.0–8.0) in various portions. For the preparation of sample solutions, 1 mL portions of the stock solution, prepared by dissolving 3–5 mg of compound **7a** in CH_3CN (20 mL), were diluted to 10 mL with the buffer solution (8 mL) and CH_3CN (1 mL). The UV–vis spectrum was recorded for cation **7a** in 20 different buffer solutions. Immediately after recording the spectrum, the pH of each solution was determined on a pH meter calibrated with standard buffers. The observed absorbance at the specific absorption wavelength (500 nm) of cation **7a** was plotted against pH to give a classical titration curve, whose midpoint was taken as the pK_{R+} value.

4.12. Cyclic voltammetry of 5a,b and 7a

The reduction potentials of **5a**,**b** and **7a** were determined by means of CV-27 voltammetry controller (BAS Co). A three-electrode cell was used, consisting of Pt working and an Ag/$AgNO_3$ reference electrode. Nitrogen was bubbled through a CH_3CN solution (4 mL) of each sample (1 mmol dm^{-3}) and Bu_4NClO_4 (100 mmol dm^{-3} to deaerate it. The measurements were made at a scan rate of 0.1 V s^{-1}, and the voltammograms were recorded on an X–Y recorder. Immediately after the measurements, ferrocene (0.2 mmol dm^{-3}) ($E_{1/2}$=+0.083 V) was added as the internal standard, and the observed peak potentials were corrected with reference to this standard.

4.13. X-ray structure determination of 6a[†]

Reddish prisms, $C_{22}H_{15}N_5O$, M=365.39, triclinic, space group $P-1$, a=7.059(3), b=10.399(5), c=11.990(7) Å, α=100.50(3)°, β=96.87(3)°, γ=105.17(2)°, V=822.2(7) Å^3, Z=2, D_c=1.476 g mL^{-1}, crystal dimensions 0.80×0.50×0.30 mm. Data were measured on a Rigaku RAXIS-RAPID radiation diffractomater with graphite monochromated Mo Kα radiation. Total 7445 reflections were collected, using the ω–2θ scan technique to a maximum 2θ value of 55.0°. The structure was solved by direct methods and refined by a full-matrix least-squares method using SIR92 structure analysis software, with 268 variables and 2897 observed reflections [$I>3.00\sigma(I)$]. The non-hydrogen atoms were refined anisotropically. The weighting scheme $w=[20.0000\times\sigma_c(F_0^2)+0.0010\times F_0^2+0.5000]^{-1}$ gave satisfactory agreement analysis. The final R and Rw values were 0.0810 and 0.0990. The maximum peak and minimum peak in the final difference map were 0.38 and −0.41 e$^-$/Å^3.

4.14. X-ray structure determination of 6b[‡]

Reddish prisms, $C_{23}H_{14}Cl_3N_7O_5$, M=574.77, monoclinic, space group $P2_1/n$, a=13.15(1), b=14.632(9), c=13.754(8) Å, β=114.06(5) °, V=2417.0(3) Å^3, Z=4, D_c=1.579 g mL^{-1}, crystal dimensions 0.80×0.40×0.20 mm. Data were measured on a Rigaku RAXIS-RAPID radiation diffractomater with graphite monochromated Mo Kα radiation. Total 21,037 reflections were collected, using the ω–2θ scan technique to a maximum 2θ value of 55.0°. The structure was solved by direct methods

[†] CCDC reference number 266692.
[‡] CCDC reference number 266693.

and refined by a full-matrix least-squares method using SIR92 structure analysis software, with 357 variables and 2922 observed reflections [$I>3.00\sigma(I)$]. The non-hydrogen atoms were refined anisotropically. The weighting scheme $w=[3.0000\times\sigma_c(F_0^2)+0.0010\times F_0^2+0.5000]^{-1}$ gave satisfactory agreement analysis. The final R and Rw values were 0.0690 and 0.0860. The maximum peak and minimum peak in the final difference map were 1.01 and -0.78 e$^-$/Å^3.

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